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INSTITUTE OF  
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THE POLYELECTROLYTE PROPERTIES OF  
GLUCURONARABOXILAN FROM  
BLACK SPRUCE

Project 2251

Report Four

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THE PIONEER RESEARCH COMMITTEE  
PIONEER RESEARCH PROGRAM

January 1964

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

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A Progress Report

to

THE PIONEERING RESEARCH COMMITTEE  
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August 31, 1964

It will be recalled that the glucuronoaraboxylan polymer (GAX) extracted from black spruce following a neutral cook, has one glucuronic acid side unit, apparently randomly placed, for each eight xylose units in the main chain of the polymer. The hemicellulose can in consequence be classed among the polyelectrolyte polymers and should reveal their characteristic properties.

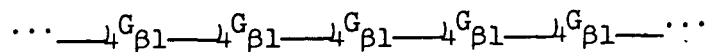
Gum arabic, an exudate from the acacia tree, which is also a uronic-acid-containing polysaccharide was chosen for comparison with the hemicellulose. The sugar contents of the two polymers is given in Table I, and its structure is compared to that of GAX and cellulose in Fig. 1. The structures of the polymers were obtained by methylation followed by hydrolysis and identification of the residual monomer units. The placement of the linkages between sugar units was then deduced (1, 2).

TABLE I  
A COMPARISON OF CARBOHYDRATE COMPOSITIONS

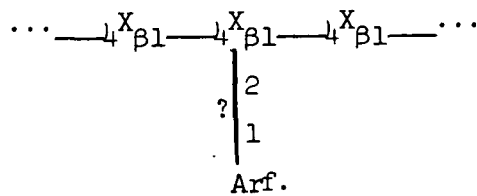
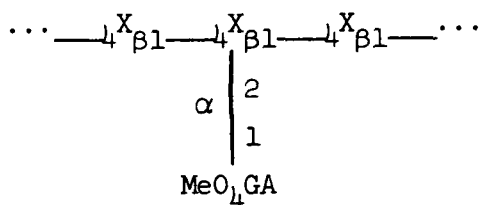
	Spruce "Xylan"	Gum Arabic
$[\alpha]_D^{25}$ (Cl, 5% NaOH)	-63.7°	-17.8°
Molar ratio of:		
Galactose	0	27
Mannose	0	0
Arabinose	0.5	21
Xylose	8.0	0
Rhamnose	0	7
4-O-Methyl-D-glucuronic acid	1.0	0
Glucuronic acid	0	6

When polyelectrolytes are dispersed in water the polar units on a single molecule repel each other causing the polymer to increase in volume and viscosity. As the concentration is lowered in the viscosity determination, crowding is relieved and expansion and the viscosity increase. This effect is shown in

CELLULOSE



4-O-METHYLGLUCURONOARABOXYLAN



GUM ARABIC

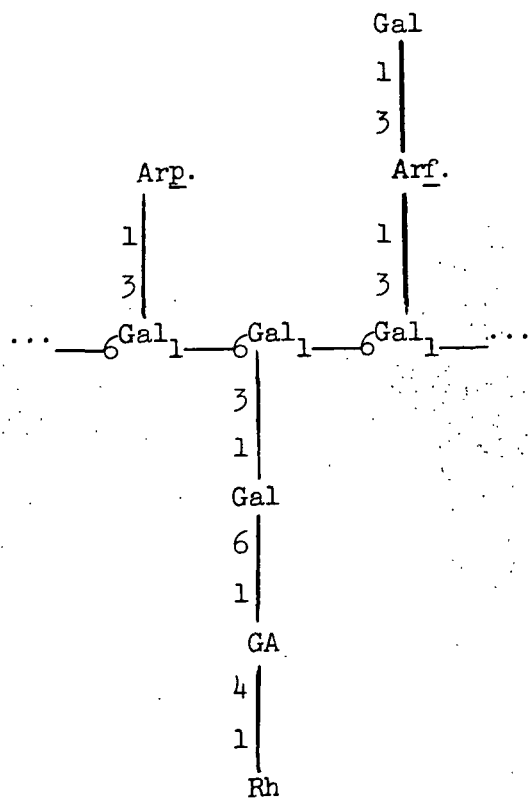


Figure 1. Structure Comparisons

Fig. 2 and 3 for gum arabic and GAX in water. If the polar groups are sufficiently neutralized with counter-ions the repelling effect is overcome and linear extrapolation of the viscosity plot is possible. This is illustrated by the use of salt and acid in Fig. 2 and 3 where the effect is seen to be much more pronounced in gum arabic than in GAX. This occurs although the gum arabic is highly branched. It appears to be due to the greater rotational freedom to be expected of the 1-6 linkages which unite the uronic acid to the galactose units in gum arabic, in comparison to the ether linkages between xylose units in the hemicellulose.

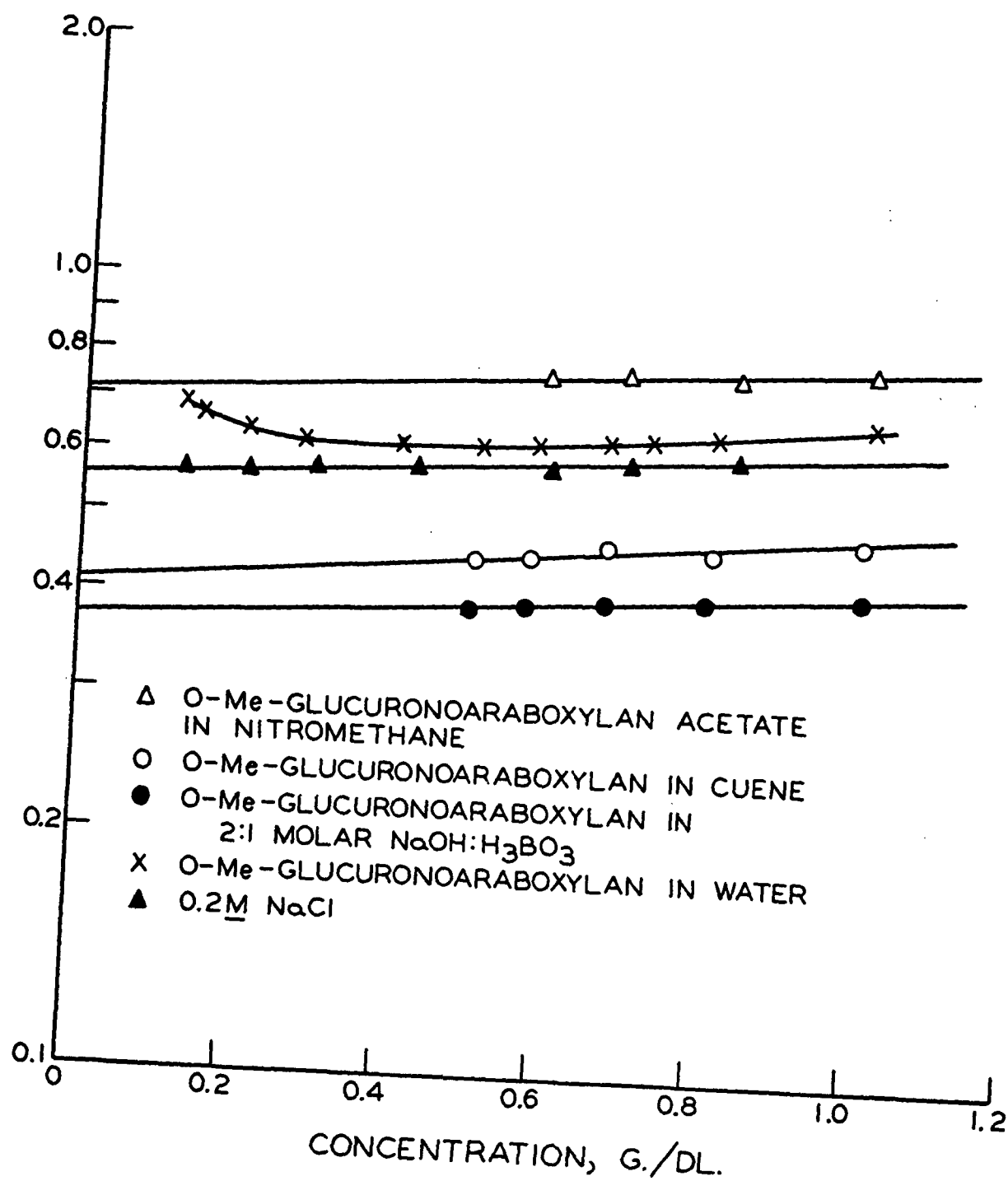


Figure 2. The Polyelectrolyte Viscosity Effect in Glucuronoaraboxyylan

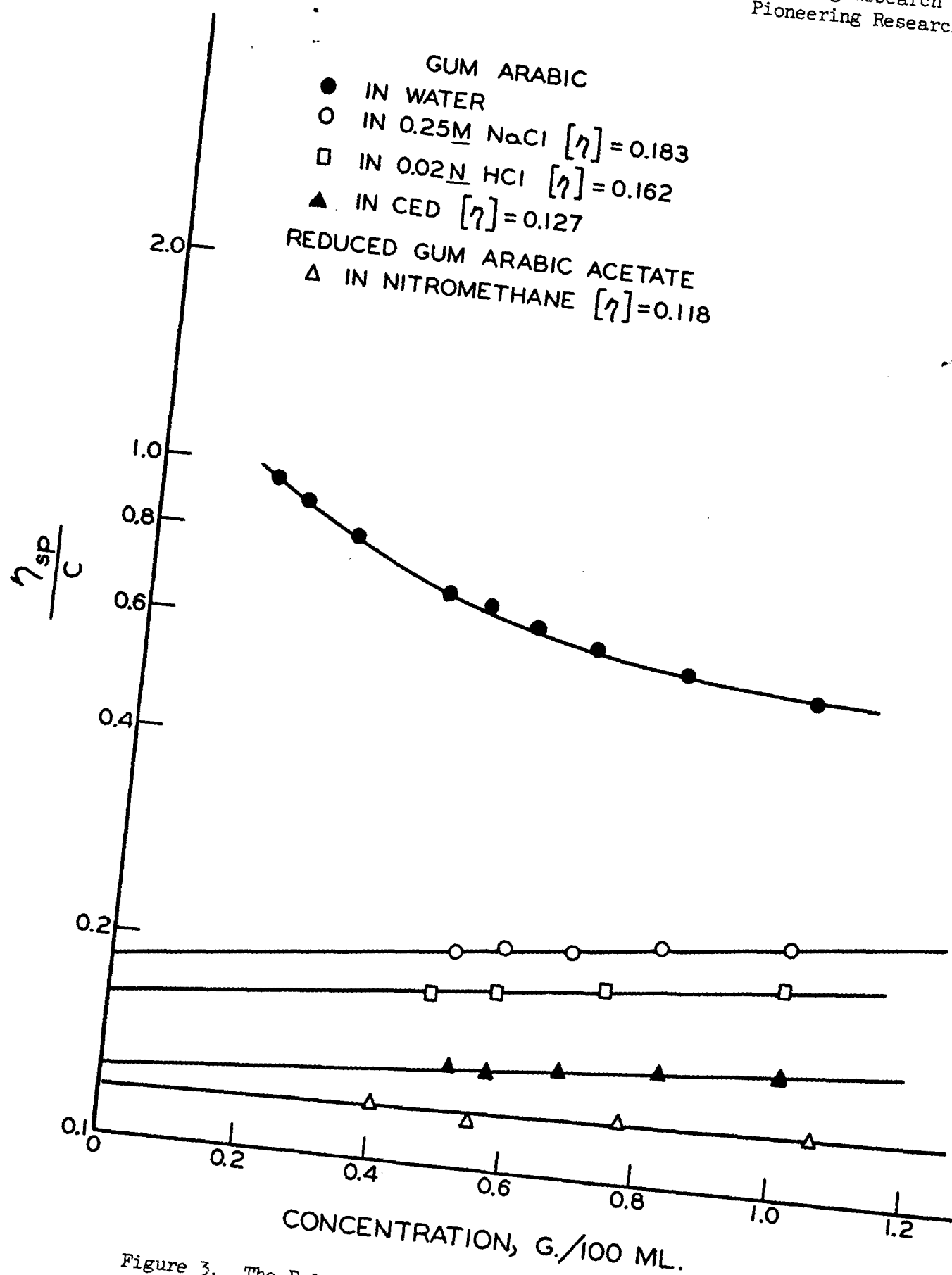


Figure 3. The Polyelectrolyte Viscosity Effect in Gum Arabic

## PREPARATION OF THE ACETYL DERIVATIVE

The polyelectrolyte effect is also overcome by preparing a derivative of the polymer after reduction of the uronic acid groups. An organic solvent can then be used. The sequence used in preparing the GAX and gum arabic acetate derivatives (3) is shown in Table II and further properties of the polymers are given in Table III. The molecular weight, mean end-to-end length in Angstroms, the extension ratio  $L/L_{\max}$  of the acetate derivatives and their comparison with cellulose of like D.P. are found in Table IV. Although the D.P. of the gum arabic acetate is ten times that of the GAX acetate, the calculated length is only slightly greater. The very low extension ratio also reflects the branched structure of gum arabic.

TABLE II  
PREPARATION OF HEMICELLULOSE DERIVATIVES

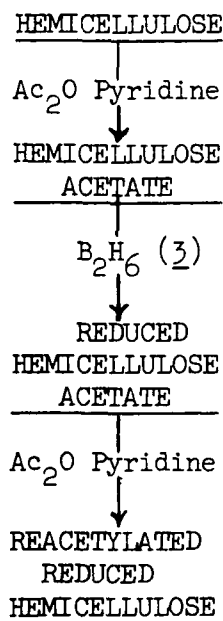




TABLE III  
CHEMICAL PROPERTIES OF ACETYLATED POLYMERS

	4-O-Methylglucuronoaraboxylan		Gum Arabic	
	Nonreduced	Reduced	Nonreduced	Reduced
Viscosity (D.M.F.)	0.54	0.54	( <sup>a</sup> )	0.118
Chromatographic test for uronic acid	positive	negative	positive	negative
$[\alpha]_D^{25}$ (Cl, CHCl <sub>3</sub> )	-70.2°	-76.2°	-9.2° <sup>a</sup>	+2.5°
Acetyl, %	38.4	--	41.9	--

<sup>a</sup>Poor solution.

Formation of the derivative appears to restrict the branched gum arabic to a minimal volume so that its viscosity in nitromethane (cf. Fig. 2) is less than that of the original polymer in cupriethylenediamine (CED). Its molecular weight has been nearly doubled because of the added acetyl groups. In comparison, the GAX acetate in nitromethane has twice the viscosity of the original polymer in CED in proportion to its increase in molecular weight. This may be because the bulk of the acetyl groups can make full contribution to the volume and viscosity on a straight chain, in contrast to a branched structure like gum arabic where the acetyl group finds place largely within the original spatial limits of the polymer. The original polymers are found to have considerably lower viscosities in CED than in salt solution. The explanation may lie in complex formation with the solvent which is known to occur (4). The high concentration of counter-ions in the highly alkaline borate solvent may also contribute.

The original research proposal stressed the importance of examining a derivative of the hemicelluloses in order to verify the analytical values obtained in the complex-forming borate solvent. The acetate derivative was chosen for the

TABLE IV  
COMPARISON OF THE MOLECULAR WEIGHT AND APPARENT SIZE OF  
O-METHYLGLUCURONOARABOXYLAN ACETATE AND REDUCED  
GUM ARABIC ACETATE

Sample	Solvent	$[\eta]$	$\frac{M}{N}$	$\frac{M}{W}$	Mon- omer Wt.	D.P. $\frac{W}{N}$	$\frac{L}{A}$	$\frac{L_{max}}{A}$	Extension Ratio $\frac{L}{L_{max}}$	Approx. $\frac{L}{L_{max}}$ of Cellulose
<u>O</u> -Methylglucurono- araboxylan	Sodium borate <sup>a</sup>	0.37		28,000	137	204	180	886	0.203	0.39 <sup>c</sup>
<u>O</u> -Methylglucurono- araboxylan acetate	Nitro- methane	0.71	26,900		227	237 <sup>b</sup>	267	1221	0.218	
Reduced gum arabic acetate	Nitro- methane	0.118	200,300	434,000	147	2952	294	15,202	0.0194	0.20 <sup>c</sup>

<sup>a</sup>A 2:1 molar ratio NaOH:H<sub>3</sub>BO<sub>3</sub>.

<sup>b</sup>Based on assumption that  $\frac{M}{W}/\frac{M}{N} = 2$ .

<sup>c</sup>At similar D.P. level.

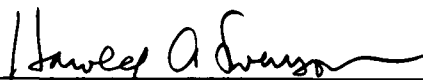
xylan hemicelluloses since it could be expected by analogy to cellulose acetate to have good solubility and can be prepared with little degradation. Mixed derivatives could have been tried but these have serious theoretical drawbacks in a study of this kind.

It was possible to determine viscosities and the number average molecular weight by osmotic pressure analysis of the GAX derivative but the weight average molecular weight could not be reliably determined either by light scattering or sedimentation analyses. One of the latter measurements is needed to properly establish the polymer size as well as the important molecular weight distribution. A large number of solvents were tried without success, among them trifluoroethanol, a powerful new solvent. Failure was due largely to apparent aggregation of the polymer in solution which seems to be peculiar to the hemicellulose acetates since it does not occur in cellulose acetate at a similar low molecular weight level. Large corrections for depolarization and fluorescence were also needed in the light-scattering determinations.

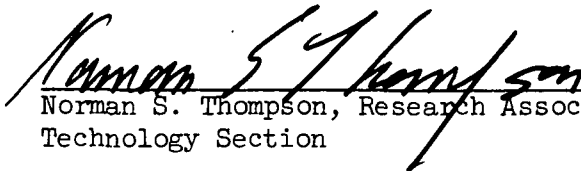
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